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Raman and photoluminescence studies on low-dimensional PbI_2 particles embedded in polymer matrix

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PbI_2 crystallite incorporated in optically transparent polyacrylamide and poly (vinyl alcohol) matrix have been studied by Raman scattering, photoluminescence (PL) at low temperature and Scanning Electron Microscopy (SEM). The small particles of PbI_2 embedded in different host matrix were prepared by: i) cooling to the room temperature a boiling saturated aqueous PbI_2 solution containing polyacrylamide or poly (vinyl alcohol) and ii) by chemical reaction of KI and $Pb(NO_3)_2$ in aqueous polyacrylamide solution. In all cases, were identified hexagonal platelets of PbI_2 and rods like particles. The rods are featured by a similar Raman spectrum and a specific green emission (cca 550 nm). Modification of the Raman and PL spectra results from a compressing effect produced by the penetration between the PbI_2 layers of different molecular species. By compression the hybridized electronic level situated at the top of valence band, formed by the contribution of the 6*s* and *5p* states of Pb^{2+} and I^- ions, undergo a deformation that induces a weakness of the interaction between the lead ion and iodine electron within a layer so that the photoluminescence of intercalated PbI_2 acquires the characteristics of Pb^{2+} emission when it is dissolved in an alkali halide crystal.

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1. Introduction

The study of optic and optoelectronic properties of low-dimensional inorganic/ organic hybrid compounds has attracted much attention in recent years [1-7]. The guest-host systems consisting of organic and inorganic components combine the wide variety of properties associated with each component.

Among the semiconductor compounds, the lead iodide is a challenging material. As an anisotropic crystal, PbI_2 have a layered structure, with repeat unit of hexagonally closed-packed layer of lead ions sandwiched between two layers of iodine ions. The bulk PbI_2 crystal is featured by a strong intralayer chemical bonding and a weak interlayer van der Waals interactions [8].

Low-dimensional lead iodide particles have been prepared in colloidal solutions [9, 10] and embedded in transparent solid media (SiO_2 [11], zeolite [12] and polymers [4,6,13,14]). Thermally stable, easy in processing and transparent to light, the polymers are an ideal host matrix for the inorganic particles. They can exert a direct influence on the semiconducting crystallite size, morphology and orientation [7].

In this paper we show that the cooling down slowly a PbI_2/polymer aqueous solution or the chemical synthesis of PbI_2 from $Pb(NO_3)_2$ and KI carried out in aqueous polymer solution, lead to the formation of the same type of particles, i.e hexagonal platelets and prismatic rods. The SEM pictures are the thought provoking. The platelets are undoubtedly PbI_2 crystalline particles having the same Raman spectrum and PL emission with those of the PbI_2 powder prepared grinding a crystalline ingot growth from the melt that was previously purified by fusion zone. The appearance of rods like particles, characterized by a specific Raman spectrum, is a result of the intercalation during the crystallization process of PbI_2 by polymer that leads to rhombohedral crystaline structures. Another common feature of rods like particles is an intense green emission (cca. 550 nm) that appears at low temperature and when the excitation is done at 334 nm.

2. Experimental

The synthesis of PbI_2 crystallites in the presence of polymer were prepared by two procedures described in [4, 6, 9] with some modifications. A method consists in the slow cooling to the room temperature of a boiling saturated aqueous PbI_2 solution in which was added prior to the cooling 0.01 % aqueous polymer (poly (vinyl alcohol) or polyacrylamide). Another method is based on the chemical reaction between KI and $Pb(NO_3)_2$ in a 0.01 % aqueous polyacrylamide solution. Into 100 cm^3 of polymer solution, under vigorously ultrasonic homogenizing, was added 5 cm^3 of 0.01 M aqueous solution of lead nitrate and then 5 cm^3 of 0.05 M aqueous solution of potassium iodide. In both synthesis methods, the sudden appearance of the yellow colour is the first evidence of the formation of PbI_2 crystallites. All materials used were of analytical grade quality.

The shape of the particles were determined by scanning electron microscopy (SEM, JEOL 200 CX).

The Raman spectra were recorded under 676.4 nm excitation light at room temperature in backscattering geometry with a Jobin Yvon T64000 spectrophotometer equipped with a microprobe allowing the laser spot to be focused on the sample within a micrometer scale. This facility has permitted an individual Raman inspection of particles of different size and shape.

The luminescence spectra at liquid nitrogen temperature (LNT) were recorded in reflection at right-angle geometry under continuous excitation using a Coherent Innova 90 argon ion laser or a Hg lamp as the excitation light sources. The emission spectrometer was a SPEX double monochromator, equipped with a cooled EMI photomultiplier and a photon counting system.

3. Results and discussion

SEM pictures in Fig. 1 show the low-dimensional PbI_2 particles embedded in polymer matrix. Fig. 1a and Fig. 1b present the particles resulted by slowly cooling to the room temperature of a hot saturated aqueous PbI_2 solution in the presence of poly (vinyl alcohol) and polyacrylamide, respectively. The particles obtained by chemical reaction between lead nitrate and potassium iodide lead carried out in aqueous water polyacrylamide solution are presented in Fig. 1c. In all cases both, hexagonal platelets of PbI_2 and rod-like particles are formed.

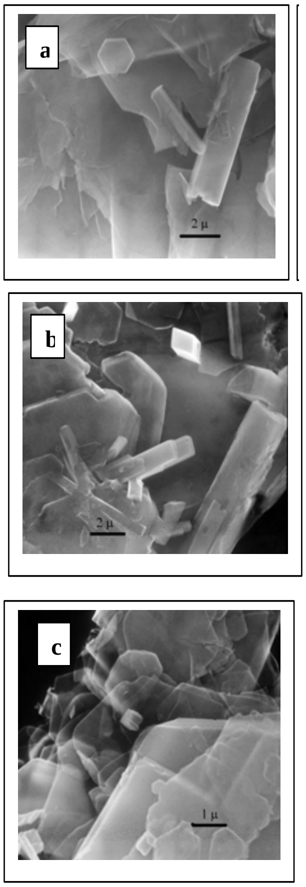

Fig. 1. SEM pictures of the particles produced by cooling to the room temperature of a hot saturated aqueous PbI_2 solution in the presence of the poly (vinyl alcohol) (a), polyacrylamide (b) and by chemical reaction of KI and $Pb(NO_3)_2$ in aqueous polyacrylamide solution (c).

It is interesting to notice that the same type of particles, i.e. platelets and rods, were produced by the chemical reaction between lead nitrate and potassium iodide carried out in different liquid as water, methanol, ethanol and acetonitrile, are reported into previous paper, [15]. Due to the great similarity of the Raman spectra of rods like particles and $CsPbCl_3$ in the *Pmma* orthorhombic structure reached at low temperature [15] we presumed that the rods could be $KPbI_3$ crystallites that belong to the same crystalline system.

Unexpected, the rods obtained by cooling to the room temperature a boiling saturated aqueous PbI_2 solution containing polymer or by chemical reaction of KI and $Pb(NO_3)_2$ in aqueous water polyacrylamide solution, present the same Raman spectra as the rods resulted from the same reaction carried out only in acetonitrile [15]. In the case of poly (vinyl alcohol), the Raman spectrum of the particles obtained by the cooling procedure present the same features. More, these spectra have the same profile with the Raman spectrum reported for the presumed $KPbI_3$ rods [15]. Fig. 2 illustrates how different are the Raman spectra recorded on individual PbI_2 platelets (Fig. 2a) appearing as hexagonal prismatic close-packed structures [15] from the reaction between $Pb(NO_3)_2$ and KI carried out in aqueous solution and the rods and exfoliated platelets, produced by the slowly cooling a boiling saturated aqueous PbI_2 solution containing polyacrylamide to room temperature and by the chemical reaction between KI and $Pb(NO_3)_2$ carried out in aqueous water polyacrylamide solution, Fig. 2b and Fig. 2c, respectively.

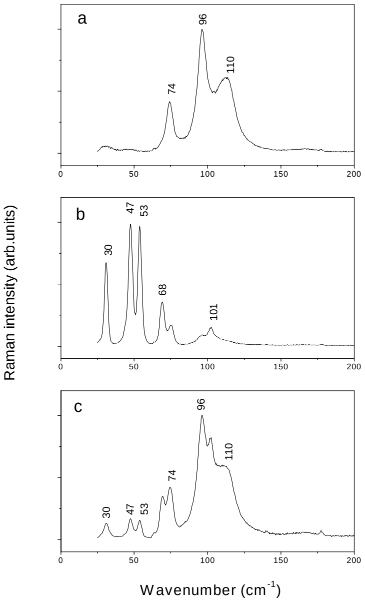

Fig. 2. Raman spectra at 676.4 nm excitation wavelengths of PbI_2 close-packed and exfoliated platelets resulted from the chemical reaction between $Pb(NO_3)_2$ and KI carried out in water and in aqueous water polyacrylamide solution (a) and (c), respectively and rods produced slowly cooling a boiling saturated aqueous PbI_2 solution containing polyacrylamide to room temperature (b).

An intercalation process of lead iodide with a polymer could explain this result. Due to the hexagonal layer structure, in the galleries between the molecular layers (into the van der Waals gap) of lead iodide can be intercalated different foreign molecules [16,17]. As it is well known, in the PbI_2 crystals the lowest conduction band is composed mainly of *6p* lead atomic orbitals. This band is extremely flat [18,19] so that it will not be affected by the c-axis expansion after intercalation. The expansion in the direction of *c* - axis transforms the crystalline structure of PbI_2 from a hexagonally packed one, with weak inter-layers van der Waals forces, in an orthorhombic structure that is featured by a quite different Raman spectrum. Such a result was already reported for the PbI_2 intercalated with ammonia and different alkyl amines [16].

The photoluminescence of the particles resulted by cooling to the room temperature a boiling saturated aqueous PbI_2 solution containing polymer (poly (vinyl alcohol) or polyacrylamide) and by chemical reaction of KI and $Pb(NO_3)_2$ in aqueous water polyacrylamide solution disclose two signatures depending on the excitation wavelength (Fig. 3).

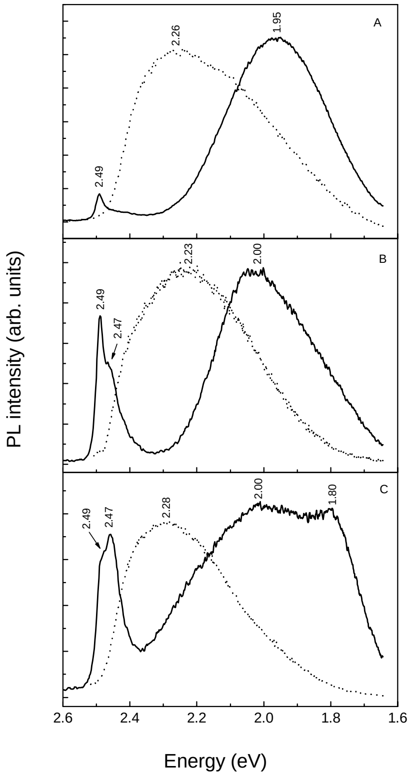

Fig. 3. Photoluminescence at liquid nitrogen temperature of the low-dimensional particles obtained by the cooling to the room temperature of a hot saturated aqueous PbI_2 solution in the presence of poly (vinyl alcohol) (A) or polyacrylamide (B) and by the reaction between $Pb(NO_3)_2$ and KI carried out in water containing polyacrylamide (C); at two excitation wavelengths: 457.9 nm (solid lines) and 334 nm (dot lines).

Normally the top of valence band of PbI_2 crystal contains an admixture of Pb^{2+} *s* and *p* and I^- *p* states [20]. Due to a compression effect resulted from the insertion of the guest molecular species between iodine layers, the hybridized electronic level situated at the top of valence band undergo a deformation by which the share of the *5p* states of I^- ions is closed down. As a result of this partition of the electronic states of Pb^{2+} and I^- ions the intra-band transition is quenched in the favour of an intra-ion one. Such a transition, revealing two bands, A_t and A_x, is clearly observed when the Pb^{2+} ions are dissolved in an alkali halide crystal [21,22].

At 457.9 nm excitation light (Fig. 3, solid lines) the PL spectrum contains an intense excitonic emission, with the maximum around of 2.5 eV, associated to the transition $3P_1 \rightarrow 1S_0$ of the Pb^{2+}. This band presents two components: one at 2.49 eV, originates in the recombination of the free excitons created by the band-to-band iradiation and another at 2.47 eV, represents the contribution coming from the recombination of the excitons trapped in the imperfections of the PbI_2 crystal lattice [15]. The dependence of the latter component for the crystal quality is observed in the Fig. 3 under laser excitation. Another component of the PL spectrum is a wide G band at about 2.0 eV interpreted as originating in a radiative electron-hole recombination process, associated with the presence of the Pb^+ ions created under band-to-band irradiation [15]. The disappearance of the G band by the simple removal of the top layer of sample indicates that it is generated in a thin layer at the crystal surface. A supplementary band, with the maximum around of 1.8 eV (Fig. 3c, solid line) is observed in the PL spectrum of sample prepared by chemical synthesis. The defects responsible for this band may be linked to the polymer presence during the chemical synthesis.

Under the excitation light of 334 nm, in the PL spectrum the excitonic emission is not more observed. In the emission spectrum appears only a wide band with the maximum at about 2.2-2.3 eV. The absence of excitonic emission means primarily that the excitation is not more suitable to form the cationic excitons, i.e. the resonant excitation of Pb^{2+} whose mixed *s* and *p* states there are in the top of valence band. The wide band originates in another excited species, linked to Pb^{2+} ions when are dispersed into alkali halide lattice. Observing Fig. 3, the question immediately arises of why, in this figure, the same samples display both types of PL spectra, one associated to the platelets or non-intercalated PbI_2 crystalline powder that are efficiently excited at 457.9 nm and another one excited at 340 nm that contains only the band at cca.2.25 eV as the typical signature of rod-like particles. An initial answer concerns our inability to perform simultaneous PL measurements on isolated particles i.e, platelets and rods of micrometric size. This can be a real inconvenience as from the preparation, powder samples regularly result that contain either platelets and rods or intercalated and non-intercalated PbI_2 particles. However, this explanation cannot be entirely accepted because in a previous paper we observed only rods when the reaction between $Pb(NO_3)_2$ and KI was carried out in acetonitrile [15]. In this context one must look for another explanation that can be associated with the non-uniformity of the rod structures, i.e. with the alternation of intercalated and non-intercalated zones in the same particle. Such a structure could be viewed as Hendricks-Teller disordered structures in which the intercalated and non-intercalated PbI_2 zones alternate [23]. With such a model a double signature of PbI_2 as semiconducting material and Pb^{2+} luminescent ion as presented in Fig. 3 is not quite unexpected. So, we are tempted to regard the emission band at cca. 2.25 eV as having the same origin as the A_x band of Pb^{2+} ion dissolved into alkali halide matrix [21, 22]. In the other words, this result suggests that in the intercalated PbI_2 the basic semiconducting properties of this material are much altered.

A quantitative evaluation of the intercalation effects is uncertain at present, it will be necessary to look in detail at the lattice structure and the stoichiometry of intercalated compounds by techniques such as X-ray diffraction, thermal analysis, etc.

4. Conclusions

We have studied by Raman scattering, photoluminescence at low temperature and Scanning Electron Microscopy, PbI_2 low-dimensional particles embedded in transparent polymer matrix. Whichever was the synthesis procedure, cooling to the room temperature a boiling saturated aqueous PbI_2 solution containing polymer or the chemical reaction of KI and $Pb(NO_3)_2$ in the presence of polyacrylamide, in both cases were identified platelets of PbI_2 and rods like particles. The luminescence and Raman signature of the rods is quite different for the one of the PbI_2 platelets. As distinct feature of the rods like particles, regardless the method used for their synthesis must be mentioned the same form, a very similar Raman spectrum and specific green emission (cca. 550 nm). The emission is observed predominantly when the excitation is done at higher energies (cca. 340 nm) at liquid nitrogen temperature. The origin of the wide band is linked to an intra-ion transition observed when Pb^{2+} ions are dispersed into alkali halide lattice.

The different optical properties of the rod-like particles are explained by a compression effect resulted from the penetration of the guest molecular species between iodine layers. Based on these data the rod-like particles are considered PbI_2 intercalated with polymer.

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